

WHAT IS CLAIMED IS:

1. An emulsion polymerization process that comprises: (1) preparing a
aqueous polymerization medium which is comprised of (a) at least one monomer, (b) a
5 polymerization control agent, and an emulsifier, wherein the emulsifier is prepared in-
situ within the aqueous polymerization medium; and (2) initiating polymerization of said
monomer within the aqueous polymerization medium.
2. An emulsion polymerization process as specified in claim 1 wherein the
10 polymerization is conducted at a temperature of less than about 250°C.
3. An emulsion polymerization process as specified in claim 1 wherein the
polymerization is conducted at a temperature of less than about 100°C.
4. An emulsion polymerization process as specified in claim 1 wherein the
15 polymerization is conducted for a sufficient period of time to result in the production of a
polymer, wherein the aqueous polymerization medium is substantially void of unreacted
initiator.
5. An emulsion polymerization as specified in claim 4 wherein at least 2
20 monomers are present and wherein the polymerization results in the production of a
block copolymer.
6. An emulsion polymerization as specified in claim 5 wherein a first
25 monomer and a second monomer are polymerized in the aqueous polymerization
medium; and wherein the second monomer is added to the polymerization medium after
substantially all of the first monomer has been converted to polymer.
7. An emulsion polymerization as specified in claim 5 wherein a first
30 monomer is copolymerized with a second monomer in the aqueous polymerization
medium, and wherein an additional quantity of monomer selected from the group
selected from the first monomer, the second monomer, and additional monomers is
added to the polymerization medium after substantially all of the first monomer and the

second monomer has been converted to polymer.

8. An emulsion polymerization as specified in claim 7 wherein the polymerization results in the production of a block copolymer.

5

9. An emulsion polymerization as specified in claim 8 wherein the number average molecular weight of the block copolymer is at least about 2,000.

10. An emulsion polymerization as specified in claim 8 wherein the number average molecular weight of the block copolymer is at least 50,000.

10

11. An emulsion polymerization as specified in claim 8 wherein the number average molecular weight of at least one block of the block copolymer is at least 25,000.

12. An emulsion polymerization as specified in claim 8 wherein the weight average molecular weight of each of a plurality of blocks in the block copolymer is at least 25,000.

15

13. An emulsion polymerization as specified in claim 8 wherein the number average molecular weight of each of a plurality of blocks in the block copolymer is at least 50,000.

20

14. An emulsion polymerization process as specified in claim 1 wherein the polymerization is a free radical polymerization and wherein the control agent is an agent for controlled free radical polymerization.

25

15. An emulsion polymerization process as specified in claim 1 wherein the emulsifier is prepared in-situ within the aqueous polymerization medium by an acid/base neutralization step.

30

16. An emulsion polymerization process as specified in claim 15 wherein the acid/base neutralization step is conducted by adding a base to a monomer solution soluble acid.

17. An emulsion polymerization process as specified in claim 15 wherein the acid/base neutralization step is conducted by adding an acid to a monomer solution soluble base.

5

18. An emulsion polymerization process as specified in claim 1 wherein the polymerization results in the production of polymer chains, and wherein at least about 50 percent of the polymer chains exhibit living polymerization kinetics.

10

19. An emulsion polymerization process as specified in claim 1 wherein the polymerization results in the production of polymer chains, and wherein at least about 80 percent of the polymer chains exhibit living polymerization kinetics.

15

20. An emulsion polymerization process as specified in claim 18 wherein the living polymerization kinetics is living free radical polymerization kinetics.

20

21. An emulsion polymerization process as specified in claim 1 wherein the polymerization results is the production of a polymer having a polydispersity of less than about 4.0.

25

22. An emulsion polymerization process as specified in claim 1 wherein the polymerization results is the production of a polymer having a polydispersity of less than about 2.0.

30

23. An emulsion polymerization process as specified in claim 1 wherein the polymerization results is the production of a polymer having a polydispersity of less than about 1.5.

30

24. An emulsion polymerization process as specified in claim 14 wherein the control agent is an agent for reversible addition-fragmentation transfer polymerization.

25. An emulsion polymerization process as specified in claim 14 wherein the control agent is an agent for atom transfer radical polymerization.

26. An emulsion polymerization process as specified in claim 14 wherein the control agent is an agent for nitroxide-mediated polymerization.

5 27. An emulsion polymerization process as specified in claim 14 wherein the control agent is an agent for degenerative transfer polymerization.

28. An emulsion polymerization process as specified in claim 1 wherein the polymerization is a ring opening metathesis polymerization and wherein the control
10 agent is an agent for controlling ring-opening polymerization.

29. An emulsion polymerization process as specified in claim 1 wherein the polymerization is an acyclic diene metathesis polymerization and wherein the control agent is an agent for controlling acyclic diene metathesis polymerization.

15 30. An emulsion polymerization process as specified in claim 1 wherein the polymerization is an anionic polymerization and wherein the control agent is an agent for controlling anionic polymerization.

20 31. An emulsion polymerization process as specified in claim 1 wherein the polymerization is a cationic polymerization and wherein the control agent is an agent for controlling cationic polymerization.

25 32. An emulsion polymerization process as specified in claim 1 wherein the polymerization is a coordination polymerization and wherein the control agent is an agent for controlling coordination polymerization.

30 33. An emulsion polymerization process as specified in claim 1 wherein the emulsifier is prepared in-situ within the aqueous medium by the reaction of a latent surfactant with a surfactant activator.

34. An emulsion polymerization process as specified in claim 33 wherein the latent surfactant is a conjugate acid of an anionic surfactant, wherein the pK_a of the acid

is less than about 14.

35. An emulsion polymerization process as specified in claim 33 wherein the latent surfactant is a conjugate base of an anionic surfactant, wherein the pK_b of the base is less than about 14.

36. An emulsion polymerization process as specified in claim 34 wherein the latent surfactant is a carboxylic acid.

37. An emulsion polymerization process as specified in claim 34 wherein the latent surfactant is a sulfonic acid.

38. An emulsion polymerization process as specified in claim 34 wherein the latent surfactant is a sulfate ester.

39. An emulsion polymerization process as specified in claim 33 wherein the surfactant activator is a hydroxide of a Group I metal.

40. An emulsion polymerization process as specified in claim 33 wherein the surfactant activator is a Group I metal phosphate.

41. An emulsion polymerization process as specified in claim 33 wherein the surfactant activator is an amine.

42. An emulsion polymerization process as specified in claim 14 wherein the free radical polymerization is initiated with a free radical initiator selected from the group consisting of peroxides, persulfates, and azo compounds.

43. An emulsion polymerization process as specified in claim 14 wherein the free radical polymerization is initiated with a redox initiator.

44. An emulsion polymerization process as specified in claim 26 wherein the control agent for nitroxide-mediated polymerization is formed in-situ from a nitron.

45. An emulsion polymerization process as specified in claim 26 wherein the control agent for nitroxide-mediated polymerization is formed in-situ from an aldehyde and a hydroxyl amine.

5

46. An emulsion polymerization process as specified in claim 14 wherein 1,3-butadiene monomer and styrene monomer are copolymerized into styrene-butadiene rubber.

10

47. An emulsion polymerization process as specified in claim 14 wherein the monomer is a conjugated diolefin monomer.

48. An emulsion polymerization process as specified in claim 14 wherein the conjugated diolefin monomer is 1,3-butadiene.

15

49. An emulsion polymerization process as specified in claim 14 wherein the conjugated diolefin monomer is isoprene.

50. An emulsion polymerization process as specified in claim 47 wherein the conjugated diolefin monomer is copolymerized with a vinyl aromatic monomer.

20

51. An emulsion polymerization process as specified in claim 50 wherein the vinyl aromatic monomer is styrene.

25

52. An emulsion polymerization process as specified in claim 50 wherein the vinyl aromatic monomer is alpha-methyl styrene.

53. An emulsion polymerization process as specified in claim 1 wherein the polymerization is carried out at a temperature of greater than about -10°C.

30

54. An emulsion polymerization process as specified in claim 1 wherein the polymerization is carried out at a temperature of greater than about 0°C.

55. An emulsion polymerization process as specified in claim 1 wherein the polymerization is carried out at a temperature of greater than about 10°C.

56. An emulsion polymerization process that comprises: (1) preparing a
5 monomer solution which is comprised of (a) at least one monomer, (b) a conjugate acid
of a surfactant with a pK_a of less than about 14, and (c) a controlled free radical
polymerization agent; (2) preparing an aqueous medium which is comprised of (a) water,
and (b) a conjugate base of a weak acid wherein the pK_b of the base is less than about 14;
and (3) mixing the monomer solution with the aqueous medium under conditions that
10 result in the in-situ formation of an emulsifier, and (4) initiating free radical
polymerization.

57. An emulsion polymerization as specified in claim 56 wherein the
controlled free radical polymerization agent is a reversible addition-fragmentation chain
15 transfer agent.

58. An emulsion polymerization as specified in claim 56 wherein the
conjugate acid of the surfactant is a carboxylic acid.

59. An emulsion polymerization as specified in claim 56 wherein the
20 conjugate base of a weak acid is a hydroxide of a Group I metal.

60. An emulsion polymerization as specified in claim 56 wherein the aqueous
medium is further comprised of a group I metal phosphate.

25

61. The polymer made by the process specified in claim 56.

62. An emulsion polymerization process as specified in claim 1 wherein the
polymerization is initiated within the aqueous polymerization medium.

30

63. An emulsion polymerization process as specified in claim 28 wherein the
ring-opening polymerization is a metathesis polymerization.

64. An emulsion polymerization process as specified in claim 14 wherein the free radical polymerization is initiated with a free radical initiator selected from the group consisting of perborates, percarbonates, and ozonides.

5 65. An emulsion polymerization process as specified in claim 56 wherein the conjugate acid of the surfactant has a pK_a within the range of 0 to 7 and wherein the conjugate base of the weak acid has a pK_b within the range of 0 to 7.

10 66. An emulsion polymerization process as specified in claim 4 wherein polymerization is initiated in step (2) with a first polymerization initiator; and wherein polymerization is subsequently initiated with a second polymerization initiator.

15 67. An emulsion polymerization process as specified in claim 66 wherein the first polymerization initiator utilizes a mechanism falling within a category selected from the group consisting of atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), reversible addition-fragmentation transfer (RAFT), degenerative transfer (DT), anionic polymerization, cationic polymerization, coordination polymerization, ring opening metathesis polymerization, (ROMP), acyclic diene metathesis polymerization (ADMET), and other polymerization reactions involving
20 stable free radicals (SFR); and wherein the second polymerization initiator utilizes a mechanism falling within a category different from that utilized by the first initiator.

25 68. An emulsion polymerization process as specified in claim 1 wherein polymerization is achieved using at least two different control agents independently selected from the group consisting of control agents for free radical polymerization, anionic polymerization, cationic polymerization, coordination polymerization, ring opening metathesis polymerization, (ROMP), acyclic diene metathesis polymerization (ADMET), and other polymerization reactions involving stable free radicals (SFR).